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Heterogeneous Chemistry in Solid Rocket Motor Plumes

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Final Report

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Summary

Reaction rates of ozone decomposition and adsorption/desorption rates of HCl on aluminum oxide (alumina) particles were measured by a new technique involving real-time ultraviolet absorption spectroscopy in a static reactor. Reaction probabilities η are reported for ozone on α -alumina, γ -alumina, and chromatographic alumina (hydroxylated alumina), respectively, over the temperature range -60 to 200°C . These measurements expand on previous measurements from this group using a flow tube reactor. The adsorption/desorption kinetics is a new effort that addresses the key issue of whether heterogeneous chemistry, such as the reaction $\text{HCl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3$, on alumina particles is a significant reaction mechanism for global stratospheric ozone depletion.

1. Introduction

This work explores the atmospheric impact of solid rocket motor (SRM) plume exhaust through laboratory measurements of key heterogeneous reaction rates. SRMs are commonly used for heavy launch vehicles because of their high thrust, relatively uncomplicated and inexpensive construction, and because they use storable propellants (as opposed to cryogenic hydrogen/oxygen liquid thrusters). SRMs are the principal boosters on the four largest classes of US lifters, namely Space Shuttle, Titan IV, Delta, and Atlas. They are also to be used by the largest ESA launcher Ariane 5. The most widely used propellant formulation consists of ammonium perchlorate (NH_4ClO_4) oxidizer and aluminum (Al) fuel with organic binder.

The USAF launches Titan IV vehicles from Vandenberg AFB and from Cape Canaveral. A single Titan IV vehicle releases about 48 tons of chlorine and about 68 tons of alumina into the stratosphere (15-60 km). The quantity of material released by the Shuttle exhaust is about 30-40% greater. There is growing concern that this exhaust may contribute to ozone depletion in the stratosphere. There have been many attempts to model the impact of solid rocket motor plumes on stratospheric ozone. Prather and collaborators investigated the long term effects using global atmospheric chemistry and dispersion models from which they concluded that at current launch rates, solid rocket motor exhaust does not impose a significant global impact on stratospheric chemistry [Prather *et al.*, 1990]. An attempt was also made to examine the transient chemical behavior and local impact. Subsequent discussions revealed a widely varying viewpoints [Aftergood, 1991; McPeters *et al.*, 1991].

Recent plume chemistry modeling has suggested that short term ozone depletion may arise along the path of SRM plumes. The principal reason is that much of the chlorine effluent is in the form of Cl_2 due to plume afterburning chemistry involving HCl and OH [Hoshizaki, 1975; Karol, 1992; Zittel, 1994; Denison *et al.* 1994]. Chemical kinetics modeling then predict extensive ozone depletion in the plume that persists for hours [Denison *et al.* 1994, Karol, 1991; Ross, 1995, Brady and Martin, 1995].

Measurements of plume composition are limited and inconclusive. A Titan III flythrough observed a 40% reduction in the ambient ozone level [*Pergament, 1977*], although this single measurement has not been repeated. McPeters, et al. [1991] presented total ozone mapping images (TOMS) as evidence that ozone depletion is insignificant in the wake of a SRM plume. However, arguments have been presented indicating that TOMS is unable to measure such an effect due to limited spatial resolution, the complicating effects of plume species that overlap with the ozone absorption spectrum [*Syage, 1995, Syage and Ross, 1996*], and uncertainty concerning plume displacement due to stratospheric winds. New Air Force flythrough measurements have been made, however, the results, to our knowledge have not been publicly disclosed.

SRM motor plumes give large quantities of aluminum oxide particle exhaust [*Brady et al. 1994*], so it is natural to consider whether heterogeneous chemistry, similar to that which occurs on polar stratospheric cloud (PSC) particles [*Solomon, 1988, Abbatt and Molina, 1992; Hanson and Ravishankara, 1991, Leu, Moore, and Keyser, 1991*], may also occur in rocket plumes. However, the plume environment differs from the Antarctic in several important ways: (1) alumina particles will probably have very different surface properties than PSCs, though adsorbed water may give rise to similar surface chemistry, (2) the stratospheric temperatures at mid latitudes are in the range of about 220-230K compared to 190-200K for the Antarctic winter, (3) the concentration of chlorine species is many orders of magnitude higher in the early plume than in the Antarctic, (4) potential for direct decomposition of ozone on alumina particles [*Hanning-Lee et al., 1996; Keyser, 1976*], and (5) in the plume, photolysis on surfaces can compete with heterogeneous thermal chemistry, in contrast to the Antarctic where heterogeneous chemistry takes place mostly during the dark polar winter. The potential for heterogeneous photochemistry on alumina particles is the subject of this paper.

The laboratory measurements presented here support atmospheric modeling efforts to understand rocket plume / stratosphere interactions. The work reported here was performed in a joint arrangement between UCLA and Aerospace and involved the efforts of Dr. Mark Hanning-Lee, a UCLA postdoc with Prof. Peter M. Felker, working at Aerospace under the super-

vision of Dr. Jack A. Syage. Aerospace facilities and resources, under AFSMC/CEV funding, contributed to this work.

2. Ozone decomposition on alumina

In this section, we present measurements of rates of ozone decomposition on aluminum oxide (alumina) particles. The purpose of this work is to examine the extent to which ozone would be depleted due to solid rocket motor (SRM) alumina particle exhaust. This question necessarily involves the coupling with other ozone depleting chemistry, such as homogeneous and heterogeneous chlorine chemistry. However, it is also important to isolate the reactivity of ozone with alumina because of the importance of evaluating (i) long-term global ozone impacts, and (ii) future propellant formulations that dispense with chlorine, but which retain aluminum.

At present, the magnitude of ozone depletion in SRM plumes is not accurately known. Chemical modeling calculations indicate the potential for significant local ozone depletion [Karol, 1992; Zittel, 1994; Denison *et al.* 1994; Ross, 1995; Brady and Martin, 1995], however, many key reaction rates are as yet still unmeasured. The importance of heterogeneous chemistry on alumina particles is also a very open question.

Properties of alumina particles in the plume, e.g., size distributions, densities, surface structure, and composition are poorly understood, yet these factors will strongly influence chemical reactivity [Beiting, 1997a,b]. Some of these properties have been studied for tropospheric alumina exhaust [Radke, Hobbs, and Hegg, 1982; Kim, Laredo, and Netzer, 1993; Strand, 1981; Cofer *et al.* 1987, 1991]. SRM plumes may consist of high densities of transient ice crystals solidified from the exhaust as neat particles or coated on alumina. The heterogeneous chemistry of these plume particles is just beginning to be examined [Lohn *et al.* 1994; Syage and Ross, 1996]. Since surface chemistry may be catalytic in nature, these particles may potentially have an impact on stratospheric plume chemistry similar to that observed in polar stratospheric clouds (PSCs) in the Antarctic.

If one assumes pseudo-first-order kinetics with respect to ozone, then reaction efficiency η can be related to rate constant k by the expression

$$\frac{d \ln[\text{O}_3]}{dt} = -k[\text{Al}_2\text{O}_3] = -\frac{v\eta\Sigma}{4}[\text{Al}_2\text{O}_3] \quad (1)$$

where v is the mean molecular speed of O_3 , Σ is the surface area per unit mass of alumina and $[\text{Al}_2\text{O}_3]$ is mass per unit gas-phase volume. The most comprehensive measurements to date appear to be those by Keyser [1977] in a JPL report. He reported reaction efficiencies measured by static and flow methods for different alumina surfaces, after adsorption of H_2O and HCl , and over a temperature range of -40 to 40°C . Keyser [1991, 1993] considered the details of diffusion and adsorption and how well ozone accesses the total surface area of porous alumina. The surface reactivities he reported of $\eta \sim 10^{-9}$ (at room temperature) are several orders of magnitude smaller than those reported by other groups. Early work by flow methods report values of $\eta \sim 10^{-5}$ [Schwab and Hartmann, 1956; Ellis and Tometz, 1972; Atiaksheva and Emelianova, 1973]. More recently Klimovskii et al. [1983] reported an ozone reactivity of $\eta \sim 10^{-4}$ at room temperature. The issue of particle porosity and effective surface area is a key issue in the present work in comparing reactivity of laboratory particles to plume alumina exhaust. Of the previous measurements of O_3 reactivity on alumina particles, only the results of Keyser and of Alebic-Juretic *et al.* [1992] allow determinations of reactivity as a function of surface area defined by the BET isotherm.

2.1. Experimental

Previous measurements of ozone decomposition on alumina particles were conducted using a flow-tube reactor equipped with a molecular beam sampling mass spectrometer and an ultraviolet/vacuum ultraviolet absorption spectrometer. The present measurements were made on a new apparatus that is better suited than a flow tube reactor for measuring slow reactions. The apparatus employs real-time absorption monitoring in a static reaction chamber as illustrated in Fig. 1. Measurements were made by injecting a reaction mixture to the chamber containing some alumina sample and measuring the rate of change of gas composition by ab-

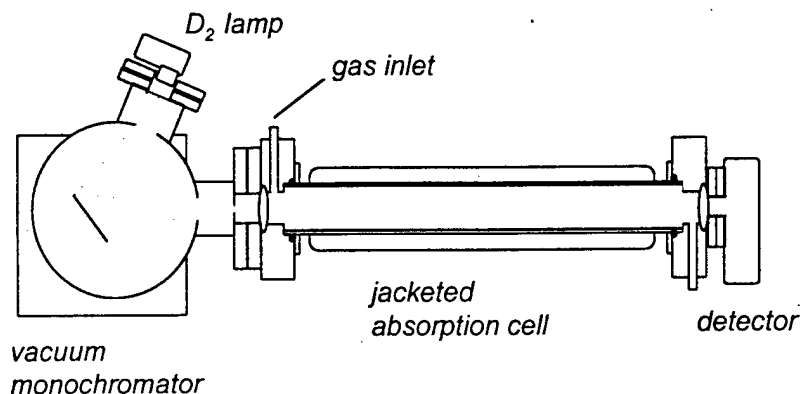


Figure 1
Schematic of the static cell kinetic absorption spectrometer. The cell is jacketed to allow measurements over the temperature range of 220 to 350 K.

sorption. The minimum reaction time is limited by the time it takes to add the reaction mixture (about 1 sec). The effective temperature range is -50°C to 100°C using temperature controlled liquid flows through the cell jacket, and up to 200°C using heating tape. The advantages of the static reaction chamber are (i) the absorption of reactant or product is followed in real-time and (ii) sample can be rapidly and efficiently changed. The disadvantage is that it is not appropriate to measuring fast reactions. The flow tube reactor and the static reaction chamber are very complementary instruments and operate well over a wide range of overlapping conditions allowing comparisons of measured reaction rates by two independent methods.

Rate constants were measured over a temperature range of -60°C to 200°C for three types of alumina: (1) α -alumina, 3 mm diam particles (Aldrich), (2) γ -alumina, 3 mm diam particles (Aldrich), and (3) chromatographic (partially hydroxylated) alumina, 0.25 mm diam particles (Alfa). Control measurements were also made in the absence of sample, which were used to correct the reported rate constants. UV absorption was typically measured at a wavelength chosen to achieve an optical density of about unity, for optimum sensitivity to small changes in ozone concentration. The mass spectrometer and UV absorption methods gave consistent results in all cases; however, the latter tended to give better reproducibility and sensitivity. Homogeneous O_3 loss is at least a factor of 10 smaller than the rates measured here. Typical kinetic traces by the flow tube and the real-time static chamber are compared in Fig. 2 to demonstrate the superior sensitivity and signal-to-noise of the latter instrument.

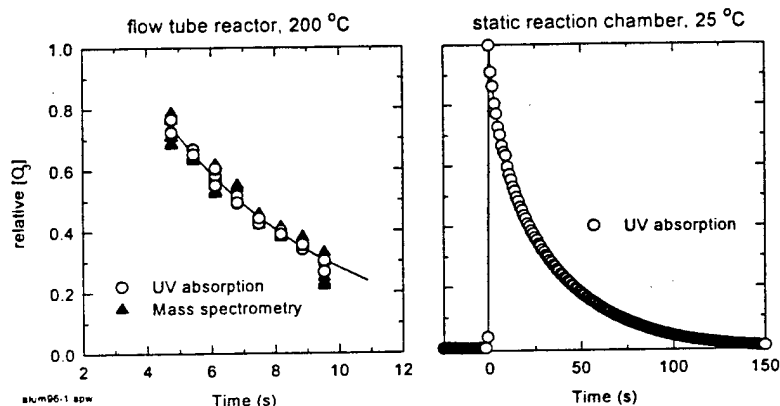


Figure 2
Comparison of kinetic measurements recorded on the flow tube and real-time reactors. Total data collection time was about 2 hr for the flow tube and 4 min for the real-time reactor.

Surface area is defined as the geometric, or outside, surface area and not the total effective surface area due to a porous structure. The geometric surface area was computed from the measured weight and known density and particle size distribution of the sample. The issue of the *effective* surface area is a difficult one to deal with. Using the chemical supplier's porosity data, the ratio of internal surface area to the geometric outside surface area is $\geq 10^4$ for chromatographic alumina. When reporting values of η , it is important to be consistent in the definition of surface area. Because we do not know the effective surface area for ozone decomposition, nor do we know the porosity of plume particles, we choose to define reactivity in terms of the simple concept of geometric or external surface area. The values of η presented here are directly applicable to calculating ozone decomposition in SRM plumes as long as we are consistent by dealing with the geometric surface area of the plume particles. This approach is fully valid for assessing the plume issue if the porosity of the laboratory and plume particles are equivalent.

2.2. Results and Analysis

Rate constants were measured over a temperature range of $-60\text{ }^{\circ}\text{C}$ to $200\text{ }^{\circ}\text{C}$ for five types of commercial alumina. Control measurements, made in the absence of sample, were used to correct the measured first-order rate constants. In the flow tube, the mass spectrometer and UV absorption methods gave consistent results in all cases; however, the latter tended to be

Table 1.
Specific Surface Areas of Alumina Particles.

| Supplier and sample | $S_{\text{BET}} / \text{cm}^2 \text{g}^{-1}$ | $S_{\text{G}} / \text{cm}^2 \text{g}^{-1}$ |
|--------------------------------|----------------------------------------------|--------------------------------------------|
| Aldrich coarse γ | 3.0×10^6 | 4.2 |
| Alfa α chips | <2600 | 3.8 |
| Aldrich α pieces | | 10 |
| Alfa chromatographic γ | 2.7×10^6 | >60 |
| Baker chromatographic γ | 2.4×10^6 | 120 |

more reproducible. Homogeneous O_3 loss is at least a factor of 10 smaller than the rates measured here. Within the experimental statistical and systematic errors, rate constants were insensitive to $[\text{O}_3]$ (5×10^{15} - $2 \times 10^{17} \text{ cm}^{-3}$) and to total pressure (8-120 torr). Decays did not deviate significantly from first order. The pressure increase during reaction is consistent with the interpretation of catalytic ozone decomposition on alumina, although this is not yet established.

The specific surface area S may be defined as the geometric or external surface area S_{G} , as the total effective surface area due to a porous structure, or as the BET area S_{BET} measured by adsorption of an unreactive gas. Values of S are presented in Table 1. To determine S_{G} it was assumed that each particle was a smooth non-porous sphere of the same density ρ as bulk α -alumina (3.96 g cm^{-3}). S_{G} was then calculated from the mean particle diameter d of the sample, using the formula $6 / (\rho d)$. S_{BET} was determined using N_2 and was at least 10^4 times higher than S_{G} for all samples studied in this work. Statistical and systematic error is $\pm 40\%$ (1σ).

Keyser *et al.* [1991] noted that the more reactive a species, the less deeply it penetrates a porous solid. Therefore the observed value of η depends on the pore size distribution. An O_3 molecule will thus sample an area intermediate between S_{BET} (determined using unreactive N_2) and S_{G} . A forthcoming publication will include a discussion of sample porosity (M. A. Hanning-Lee *et al.*, 1997a). For all samples, N_2 adsorption was at least as fast as O_3 removal, so S_{BET} is considered to represent accurately the true surface area sampled by O_3 . Because particle porosity is not always well-determined, we choose to compare activity in terms of the simple and consistent concept of BET area.

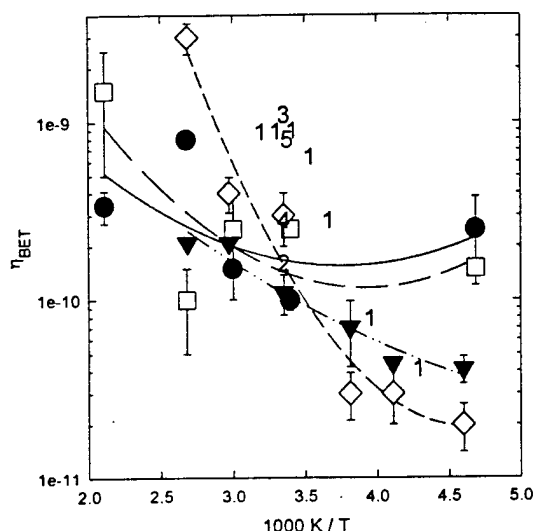


Figure 3.

Temperature dependence of ozone reactivity on alumina particles. Quadratic fit is for visualization only. Error bars reflect statistical 1s error. Values for α chips are lower limit. Key: 1-4 Keyser samples A-D, 5 Alebic-Juretic *et al.* [1992]. ●: flow tube coarse γ . □: flow tube chromatographic γ . ▼: static cell coarse γ . ◇: α chips.

Results of kinetics measurements of ozone decomposition on various types of alumina are plotted in Figure 3. From Equation 1, it may be seen that the value derived for η is inversely proportional to the value of S chosen. Thus for coarse γ -alumina at 22 °C, $\eta_{\text{BET}} = 2 \times 10^{-10}$ but $\eta_G = 1.4 \times 10^{-4}$. At -60 °C α -alumina is slightly less active than the various forms of γ -alumina. Preliminary measurements on γ -alumina saturated with HCl show that HCl reduces the rate of ozone decomposition especially at lower temperatures, possibly by binding to alumina surface sites that decompose ozone. Experiments for H_2O adsorption show a similar deactivation of ozone decomposition. In an early SRM plume, alumina is expected to become coated with HCl and H_2O . However, as the plume disperses, some of these species may desorb.

Arrhenius plots of η are curved. The plateau, and in some cases increase, in rate at low temperatures may be due to longer residence times of adsorbed O_3 . The results measured here differ in some respects from those reported by Keyser [1976], who did not observe the upturn in rate at lower temperature and the reduced rate for HCl saturated particles.

3. HCl Adsorption on alumina

The role of heterogeneous reactions, such as those associated with polar stratospheric cloud PSC particles that lead to extensive ozone depletion in the Antarctic, may also occur on alumina particles. The importance of these reactions affects the rate of chlorine activation in

the global stratosphere and could have an effect on the ozone balance. The heterogeneous reaction that is most likely to play a significant role is:



The reaction efficiency of this reaction is being conducted in the Molina lab [Molina *et al.*, 1997]. However, to apply the measured laboratory rates to the stratosphere requires understanding the fraction of HCl that is adsorbed on particles of alumina. Consequently the adsorption/desorption kinetics of HCl on alumina was measured in order to calculate the equilibrium surface coverage of alumina in the ambient stratosphere.

3.1. Experimental Method

The real-time absorption spectrometer in Fig. 1, used to measure O_3 decomposition on alumina, was also used to measure the HCl/alumina adsorption/desorption kinetics. In the latter experiment gaseous HCl was introduced into the chamber, containing alumina, in controlled amounts ($P \times V$) using a plenum volume filled to a specific pressure. The HCl pressure was measured by HCl absorption was monitored at 170 nm and by a fast baratron (capacitance manometer). The signal monitors gaseous HCl; hence the signal rises rapidly due to the addition and then decays to a plateau level. Success additions of HCl were made until the surface reached saturation. An example of time-resolved measurements and the approach to surface saturation as manifested by the rising signal plateau is given in Fig. 4

3.2. Results and Analysis

The basic kinetics for surface adsorption/desorption of gas-phase molecules is represented by the process



where x (cm^{-3}) is the gas-phase density of X, s (cm^{-3}) is the density of vacant surface sites Su per unit gas-phase volume, and x_s is the density of adsorbed $\text{X} \cdot \text{Su}$ per gas-phase volume. The

rate coefficients k_a ($\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and k_d (s^{-1}) refer to adsorption and desorption, respectively. The time dependence of x and x_s is described by the rate equations

$$\frac{d}{dt}x = -\frac{d}{dt}x_s = -k_a x(s - x_s) + k_d x_s \quad (4)$$

In general, the analytical closed form solution of Eq. (4) is complicated. The time dependence simplifies to exponential behavior under two limits: (1) large excess of either x or s , or (2) exact stoichiometric proportion of x and s . For other situations, a pseudo-exponential dependence holds if x and s are not far from their equilibrium values. In an experiment that exerts small perturbations from equilibrium, the following time dependence is valid:

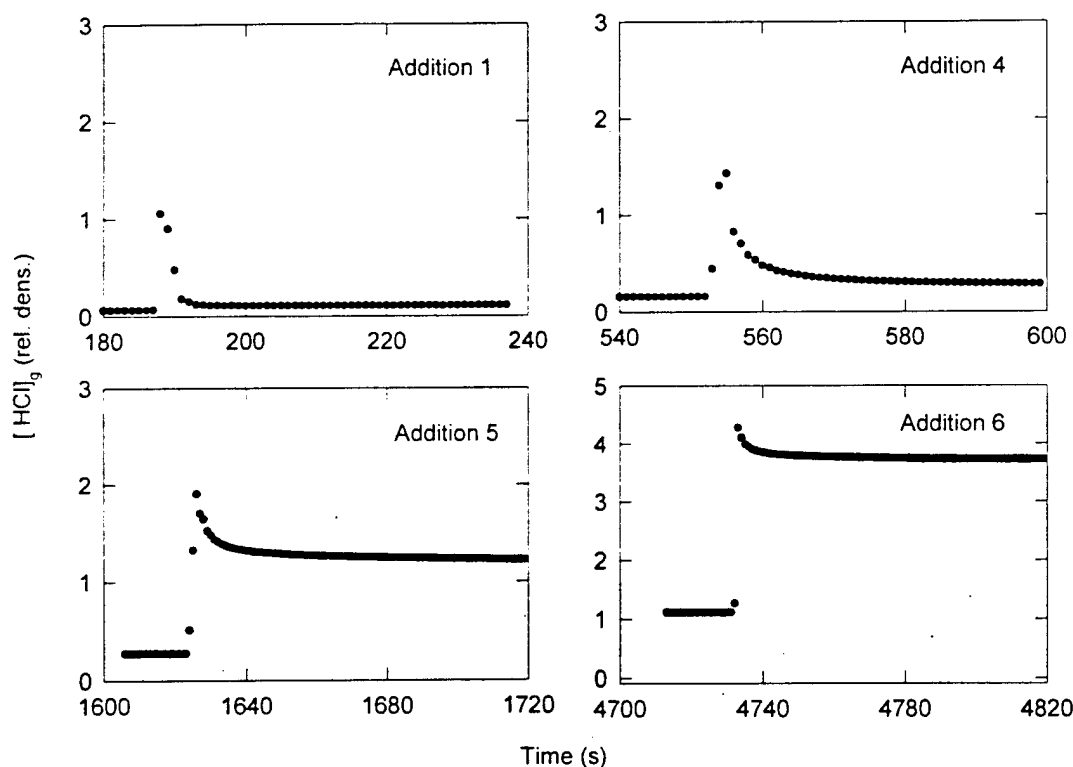


Figure 4.

HCl pressure (torr) vs time (s) for successive impulse additions of a fixed plenum volume of HCl into a reaction cell containing alumina particles. The series of traces show the time dependence and approach to surface saturation. Vertical and horizontal scales vary from plot to plot.

Table II.

Adsorption/desorption parameters for HCl/alumina as a function of temperature.

| Temperature | $k_a / 10^{-16} \text{ cm}^3 \text{ s}^{-1}$ | Sticking coefficient α | $K / 10^{-17} \text{ cm}^3$ |
|-------------|----------------------------------------------|--------------------------------|-----------------------------|
| 23 °C | 1.8 ± 0.7 | $(6.0 \pm 2.3) \times 10^{-6}$ | 4.8 ± 0.4 |
| -20 °C | 2.8 ± 2.3 | $(9.3 \pm 7.7) \times 10^{-6}$ | 7.9 ± 1.1 |
| -60 °C | 4.7 ± 3.7 | $(1.6 \pm 1.2) \times 10^{-5}$ | 10 ± 2 |

$$x(t) - x_{eq} = [x_0 - x_{eq}] \exp\left[-k_a(x_{eq} + s_{eq}) + k_d\right]t \quad (5)$$

Solving for the equilibrium values leads to the Langmuir isotherm equation for fractional surface coverage at equilibrium given by

$$\theta = \frac{Kx_{eq}}{1 + Kx_{eq}} \quad (6)$$

where $K = k_a/k_d$, and x_{eq} is the equilibrium gas-phase density.

The equilibrium constant K was measured for different types of alumina particles as a function of temperature using a real-time kinetics apparatus. A fixed quantity of HCl was pulsed injected into a chamber containing a known surface area of alumina particles, and the HCl uptake rate was measured by the change in the gas-phase vacuum ultraviolet absorption signal and by the pressure in the reaction chamber. The rate and fractional uptake could be measured, providing a cross check to the determination of K . The details of the measurement and the analysis are to be published [Hanning-Lee and Syage, 1997b]. For sub-200 μ particles of dry chromatographic alumina, a value of $K = 1 \times 10^{-16} \text{ cm}^3$ was measured at 220 K. The value of K is a function of surface coverage; the quoted value is for a sparsely covered surface. A tabulation of adsorption/desorption kinetics as a function of temperature are shown for the chromatographic alumina sample.

4. Summary and Conclusion

Rates of ozone decomposition on aluminum oxide particles were measured using a new direct time-resolved instrument for measuring rates of heterogeneous reactions. These measurements complemented earlier work from this lab using a flow tube reactor equipped with molecular beam sampling mass spectrometry and ultraviolet absorption spectroscopy. The new apparatus was also used to measure adsorption/desorption kinetics of HCl on alumina. These measurements are needed to predict the effect on the global ozone balance due to heterogeneous chemistry on aluminum oxide particles resulting from solid rocket motor exhaust.

Modeling efforts are now in progress to incorporate these measurements into an assessment of global ozone impact.

5. Acknowledgements

The results presented here were performed in a joint arrangement between UCLA and Aerospace and involved the efforts of Dr. Mark Hanning-Lee, a UCLA postdoc, working at Aerospace under the supervision of Dr. Jack A. Syage. Aerospace facilities and resources, under AFSMC/CEV funding, contributed to this work.

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